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Materials Today: Proceedings 4 (2017) 4561–4566

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INESS 2016

Local electrical properties of PTB7 film

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Abstract

A study of the spreading of currents and current-voltage characteristics in a pure PTB7 thin film by atomic force microscopy (AFM) technique was carried out in order to investigate the processes of transport of positive charge carriers in the nanoscale range. It was showed that the numerical values of the carrier mobility can significantly differ on the nanoscale and require correct interpretation of processes with the scale that are comparable with the morphological features of organic solar cells.
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Keywords: Organic photovoltaic solar cells; PTB7; the mobility of the charge carriers

1. Introduction

Organic photovoltaic solar cells (OPV) are attracted a significant number of research groups. OPV can be produced by simple production processes such as roll-to-roll processing, extrusion coating, spray coating, screen printing, inkjet printing, and so on. OPV efficiency depends crucially on the nanoscale organization of the photoactive layer and the overall architecture of these devices [1-3].

It is known that the morphology of organic photovoltaic cells effect on performances of OPV [4-9]. One of the key factors determining the performance of solar cells based on the bulk heterojunction mixture of conjugated polymers and fullerene is the stability of the structural, morphological and electrical properties of the components [10-14].

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Currently, one of the most intensively studied polymers is polythieno [3,4-b]-thiophene-co-benzodithiophene (PTB7). PTB7 combines various required physical properties, which makes it an excellent donor material for OPV [15, 16].

However, studies show that the morphology of pure PTB7 is non-uniform enough [10] and is characterized by the presence of crystalline and amorphous phase [17] which should certainly affect the photoinduced hole transport processes. Crystal grain sizes in PTB7 [9] have characteristic dimensions comparable to the diffusion length of excitons 4-20 nm [18] and it is expected that the structural nonuniformity will significantly influence on both the processes of hole transport in the PTB7 matrix and the efficiency OPV based on PTB7.

To study the processes of transport of positive charge carriers in the nanoscale range comparable to the morphological features of the bulk heterojunction, we carried out the study of current spreading and current-voltage (IV) characteristic in the pure PTB7 via conductive atomic force microscopy

Atomic force microscopy (AFM) and conductive AFM (C-AFM) examine surface and electronic properties within domains of nanoscale dimensions. C-AFM is a scanning probe technique, which examines surface topography and local current simultaneously and can provide information on the nanoscale charge transport properties within local domains. In these measurements, the conducting probe makes contact at different locations of the sample, and a tip acts as a nano electrode to measure current as a function of applied voltage. One can thereby obtain current-voltage (I-V) curves at different sample locations to examine charge transport and calculate the numerical value of the mobility of the majority charge carriers within domains of nanoscale dimensions.

2. Experiments and results

The configuration of the studied samples includes a glass coated with indium tin oxide (ITO)/spin-coated layer of PEDOT:PSS (Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate), hole transport layer)/spin-coated PTB7 layer. All spin-coated processes were performed in a glove box. Glass plates (2x2 cm) coated with ITO (10-15 ohm/cm2) was used as substrates. The substrates were washed with acetone, isopropyl alcohol and deionized water in ultrasonic bath and dried by nitrogen flow. PEDOT:PSS with thickness of 30-40 nm was deposited on the cleaned substrate by spin-coating and annealed in a nitrogen atmosphere at a temperature of 150^{o}C for 5 minutes to improve the film structure and electrical transport properties. PTB7 was also deposited by spin-coating technique. In the last step the samples were annealed for 15 min. under a nitrogen atmosphere at a temperature of 150^{o}C.

Spreading current measurements were performed in contact mode with Au conductive tip at a voltage of 0.5 V. Figure 1 shows the current distribution on the surface of the PTB7 film. Current distribution is correlated with the topography of the surface when a positive voltage is applied to the tip. The observed nonuniformity of current (see figure 2) reflects the impact of different processes on the transport of positive charge carriers in PTB7.

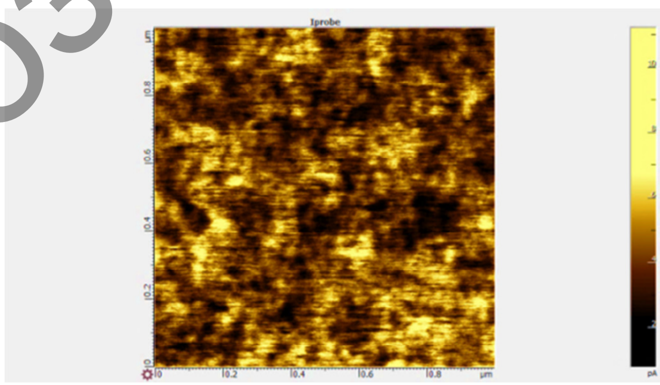

Fig. 1. Current distribution on PTB7 surface from the area of 1x1 µm at voltage of+0,5V.

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Comprehensive information on the electrical properties of the surface can be obtained by IV measurement. Curves I-V straightens in double logarithmic coordinates (see figure 3) with an exponent of 2,2 ± 0,2 which indicates that a flow is space-charge-limited current under the influence of Frenkel effect [19].

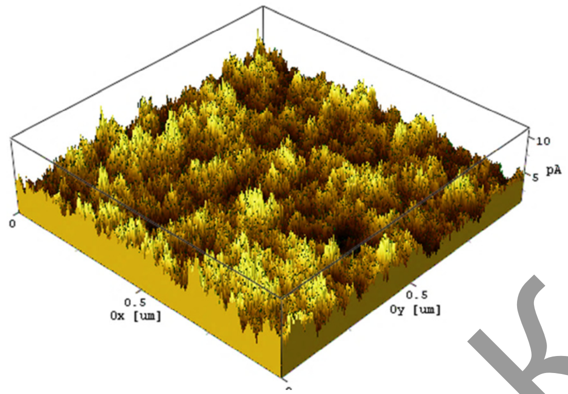

Fig. 2. 3D c-AFM raster view of PTB7 surface at voltage +0,5V.

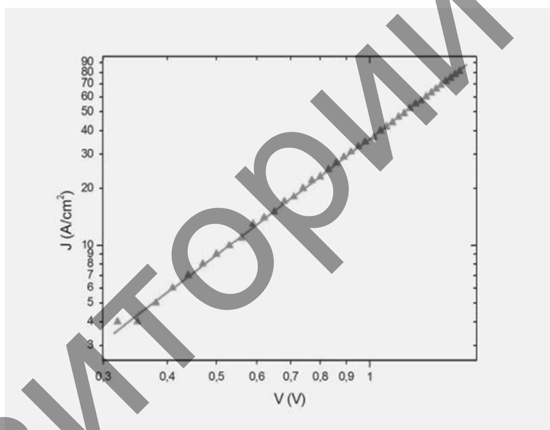

Fig. 3. c-AFM current density-voltage (J-V) curves from area of 1x1 μm (20x20 pixels), PTB7.

The dependence of the current (I) on the applied voltage (V), in this case, is described by semi-empirical equation [20]:

$$I = A_{eff} \cdot \alpha_0 \cdot \mu \cdot e^{0.89\gamma\left(\frac{V}{L}\right)^{\frac{1}{2}}} \frac{V^2}{L^3} \delta \left(\frac{L}{d}\right)^{1.6\pm0.1} \quad (1)$$

where A_{eff} is the tip-substrate contact area, α is the prefactor (α = 8.2), δ is an empirical dimensionless parameter (δ = 7.8), γ expresses the apparent field dependence (or charge density dependence) of the mobility, d is the diameter of the tip-substrate contact area, ε0 is the relative permittivity, ε is dielectric constant (ε=3, in the case of PTB7), μ is carrier mobility, L is sample thickness.

The tip-substrate contact area (A_{eff}) can be calculated using the Hertz model, where the radius of the tip-substrate contact area is defined by [21]:

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$$a = \left(\frac{3FR}{4\left(\frac{1-\nu_1^2}{Y_1} + \frac{1-\nu_2^2}{Y_2} \right)} \right)^{\frac{1}{3}} \qquad (2)$$

where F is pressing force of the tip to the sample surface, R is radius of curvature of the tip; ν is Young's modulus, Y - Poisson's ratio. When F is equal to 20 nN, R = 35 nm, Y_1=79 GPa, ν_1=0.44 for Au and Y_2 = 3 GPa, ν_2 = 0.35 for the polymer, the tip-substrate contact area A_{eff} is 92 nm^2. After taking the logarithm of (1) we obtain the following equation:

$$\ln\left(\frac{I L^{1.4} d^{1.6}}{A_{eff} V^2} \right) = 0.89\gamma \left(\frac{V}{L} \right)^{\frac{1}{2}} + \ln\left(\alpha \cdot \varepsilon_0 \cdot \varepsilon \cdot \mu \cdot \delta \right) \qquad (3)$$

I-V curves linearize in the coordinates $\left(\frac{V}{L} \right)^{\frac{1}{2}} = f\left(\ln\left(\frac{I L^{1.4} d^{1.6}}{A_{eff} V^2} \right) \right)$. The mobility of the charge carriers is determined by the line segment ln $(\alpha\ \varepsilon_0\ \varepsilon\ \mu\ \delta)$ (Fig.4) [21].

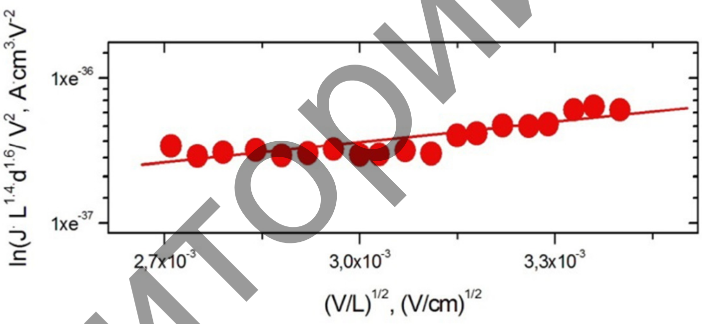

Fig. 4. The dependence of the calculated values of average c-AFM current density-voltage curves on the ratio of voltage to the thickness of the sample (see formula 3) obtained from a 1x1 µm (20x20 pixels). PTB7.

Table 1. Average Mobility Values Obtained by Eq.1 to the Experimental J-V Curves for Each Polymer, γ-field dependence (or charge density dependence) of the mobility σ-standard deviation of mobility values ($\sigma = \sqrt{\frac{\sum_{i=1}^{n} \left(\mu - \bar{\mu}\right)^2}{n}}$, n=25, $\bar{\mu}$-average value of mobility), V-variations in hole mobility ratio $\left(V = \frac{\sigma}{\bar{\mu}}\right)$:

	μ ($cm^2\ V^{-1}\ s^{-1}$)	γ $(V/cm)^{1/2}$	σ ($cm^2\ V^{-1}\ s^{-1}$)	V
PTB7	$2{,}5 \cdot 10^{-4}$	$4.3 \cdot 10^{-4}$	$6.4 \cdot 10^{-5}$	0.256

The obtained values correlate well with the results of the mobility of holes in pure PTB7 estimated by other methods [23, 25].

It should be noted that the analysis of obtained data at the surface of PTB7(0,5x0,5 µm, 20x20 pixels) reveals (see figure 5) a different type of I-V characteristics.

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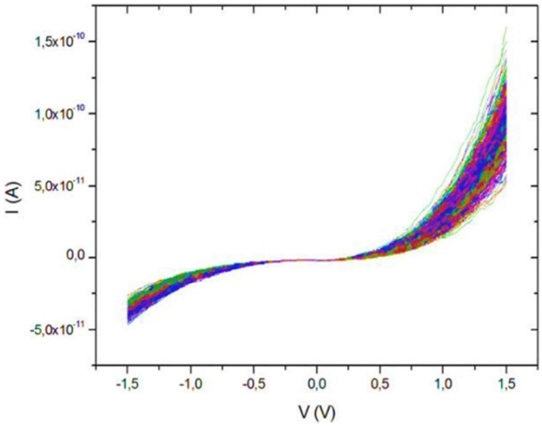

Fig. 5. c-AFM I–V curves of PTB7, at the square 500 x 500 nm, (400 dots).

High values of roof-mean-square deviation and variation coefficient of the hole mobility in pure PTB7 (table 1.) may be due to nonuniformity of the structure of the polymer films, namely the presence of the amorphous and crystalline phase [9,10,17]. Nonuniformity of the current distribution on the surface of pure PTB7 clearly indicates that the structure of the PTB7 films is not uniform (Figure 1).

Our results show that the values of the carrier mobility measured in a plane geometry average over a larger area and the interpretation of the numerical values of carrier mobility requires correct use at the nanoscale range.

Acknowledgements

Authors gratefully acknowledges the Ministry of Education and Science of the Republic of Kazakhstan for the support of this work (program Ministry of Education and Science of Kazakhstan "NU-LBNL" 0115PK03029 and Grant no.535-F-15).

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